ARKIV FÖR FYSIK Band 18 nr 39

Communicated 14 September 1960 by E. Hulthén and E. Rudberg

An electronic computer (BESK) program for one-electron two-centre integrals of Hartree–Fock self-consistent field functions in analytical form

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Although many tables of integrals occurring in quantum chemistry work have been published [1, 2, 3], their application is, as a rule, limited to calculations involving Slater functions, so that the use of Hartree–Fock self-consistent field (SCF) functions in analytical form necessitates recourse to other means of computation. The early Slater method [4] of transforming numerical SCF functions into analytical form has been greatly improved by Löwdin & Appel [5], who introduced a method of successive approximations for the expansion of a given SCF function $f(n, l) = r \cdot R(n, l)$ in exponentials

$$f(n,l) = r^{l+1} \prod_i (r_i - r) \sum_m A_m \exp(-a_m r); \quad \int_0^\infty f^2(n,l) \cdot dr = \frac{1}{C^2(n,l)},$$

where $R(n, l)$ = the radial part of the complete wave function;
n = the principal quantum number;
l = the azimutal quantum number;
i = index taking the integral values satisfying the inequality $0 < i \leqslant n - l - 1$;
r_i = the ith zero point of $f(n, l)$;
A_m, a_m = constants giving the best fit;
$C(n, l)$ = normalization constant.

Making use of the Aitken iteration scheme [6] for a simple and accurate determination of the zero points r_i of the numerical SCF functions, the tabulated values, after division by the polynomial $r^{l+1} \prod_i (r_i - r)$, represent a nodeless and monotonous function, expressible as a sum of exponentials. The method, correctly used, leads to an almost perfect fit ($f_{\text{anal}} - f_{\text{tabul}} = \pm 0.001$–$002$). It can be shown that these analytical wave functions give rise to the same general form of integrals as those involved in calculations with Slater functions, the contributory terms, however, differing in magnitude in the two cases.

In this note an electronic computer (BESK) program is described, which permits the computation of the following one-electron two centre integrals

Overlap integral: $\int \psi_A \psi_B \, d\tau$ $\qquad n_A + n_B \leqslant 9$

Moment integral: $\int \psi_A z \psi_B \, d\tau$ $\qquad 8$

Resonance integral: $\int \psi_A \frac{1}{r_A} \psi_B \, d\tau; \; \int \psi_A \frac{1}{r_B} \psi_B \, d\tau$ $\qquad 10$

Kinetic energy integral: $\int \psi_A (-\tfrac{1}{2}\Delta) \psi_B \, d\tau$ $\qquad 11$

Nuclear attraction integral: $\int \psi_A \frac{1}{r_B} \psi_A \, d\tau; \; \int \psi_B \frac{1}{r_A} \psi_B \, d\tau,$ $\qquad 10$

where the indices refer to atoms A and B respectively, according to Fig. 1. The rather modest restriction imposed on the principal quantum numbers n_A and n_B can, if needed, be removed by simple changes of the program.

The calculations are as usual made by means of spheroidal coordinates in atomic units having the following properties

$$\xi = \frac{r_A + r_B}{\varrho} \qquad 1 \leqslant \xi \leqslant \infty \qquad \varrho = \text{internuclear distance}$$

$$\eta = \frac{r_A - r_B}{\varrho} \qquad -1 \leqslant \eta \leqslant +1 \qquad 0 \leqslant \phi \leqslant 2\pi \qquad \phi = \text{the azimutal angle}$$

$$r_A \cdot r_B = \tfrac{1}{4}\varrho^2 (\xi^2 - \eta^2)$$

$$r_A \cos \vartheta_A = \tfrac{1}{2}\varrho (1 + \xi\eta)$$

$$r_B \cos \vartheta_B = \tfrac{1}{2}\varrho (1 - \xi\eta)$$

$$r_A \sin \vartheta_A = r_B \sin \vartheta_B = \tfrac{1}{2}\varrho \sqrt{(\xi^2 - 1)(\eta^2 - 1)}$$

$$d\tau = \tfrac{1}{8}\varrho^3 (\xi^2 - \eta^2) \, d\xi \, d\eta \, d\phi.$$

The various molecular integrals considered in this work can be given the common form

$$J_N = K_N \sum_{\varkappa} k_{\varkappa} \sum_{\lambda} c_{\lambda} [A_{\mu}(\gamma_{\varkappa}) \cdot B_{\nu}(\delta_{\varkappa})]_{\lambda},$$

where N = a number labelling the integral

$$K_N, \, k_{\varkappa}, \, c_{\lambda}, \, \gamma_{\varkappa}, \, \delta_{\varkappa} = \text{constants}$$

$$A_{\mu}(\gamma_{\varkappa}) = \int_1^{\infty} \xi^{\mu} \cdot \exp(-\gamma_{\varkappa}\xi) \, d\xi,$$

$$B_{\nu}(\delta_{\varkappa}) = \int_{-1}^{1} \eta^{\nu} \cdot \exp(-\delta_{\varkappa}\eta) \, d\eta$$

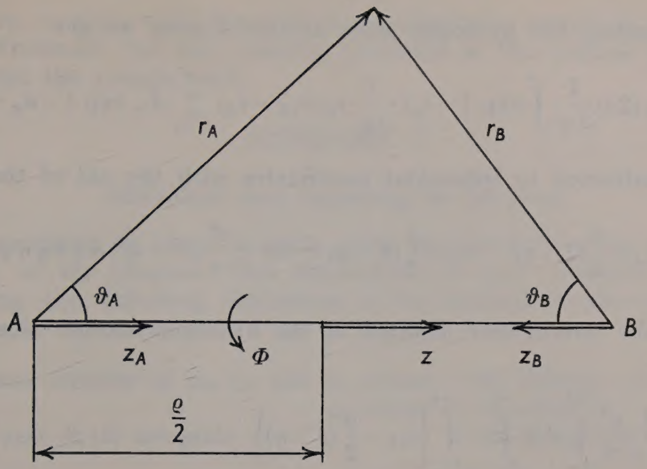

Fig. 1.

and $[A_\mu(\gamma_\varkappa)\cdot B_\nu(\delta_\varkappa)]$ represents a sum of products $A_\mu B_\nu$, the rule of summation being determined by the complete expression for the particular integral under consideration (cf. example below).

The well-known molecular functions $A_\mu(\gamma)$ and $B_\nu(\delta)$ are given in tables of molecular integrals and may be calculated in different ways (see e.g. Kotani *et al.* [1], Corbató [7], Flodmark [8], Miller *et al.* [3]). In calculating the $B_\nu(\delta)$ function a difficulty arises due to the slow convergence of this function for low values of $|\delta/\nu|$. This has been avoided in the present work by the use of a recursion formula for high values of $|\delta/\nu|$ and a series expansion for low ones. Details are given in Appendix I.

In order to exemplify an explicit form of the common integral expression we shall consider one of the integrals, which appear in calculating the overlap between hybrid orbitals of hydrogen and fluorine. Thus consideration of the 1 *s*-orbital of hydrogen and the 2 *s*-orbital of fluorine gives the following integral

$$S_N = \int \psi_H(1s)\,\psi_F(2s)\,d\tau.$$

The complete wave functions are expressed by

$$\psi_H(1s) = \frac{1}{\sqrt{\pi}}e^{-r}$$

$$\psi_F(2s) = \frac{1}{\sqrt{4\pi}}\frac{1}{r}f_F(2s),$$

$f_F(2s)$ being a normalized SCF function given analytical form according to Löwdin & Appel [5] from numerical data given by Brown [9].

$$\begin{aligned} f_F(2s) &= C_F(2s)\cdot r\,(0.25358-r)\,\{3.6103\exp(-1.9323\,r)+22.566\cdot\exp(-3.4577\,r) \\ &\quad +18.600\cdot\exp(-6.4336\,r)\} \\ &= C_F(2s)\cdot r\,(r_1-r)\sum_{m=1}^{3}A_m\cdot\exp(-a_m\cdot r). \end{aligned}$$

Arbitrarily putting the hydrogen atom as the A-atom we get

$$S_N = C_F(2s)\frac{1}{2\pi}\int \exp(-r_A)\cdot\frac{1}{r_B}\cdot r_B\,(r_{1B}-r_B)\sum_{m=1}^{3} A_m \exp(-a_m\cdot r_B)\,d\tau,$$

which is transformed to spheroidal coordinates with the aid of the relations

$$r_A = \frac{\varrho}{2}(\xi+\eta) \qquad r_B = \frac{\varrho}{2}(\xi-\eta) \qquad d\tau = \frac{\varrho^3}{8}(\xi^2-\eta^2)\,d\xi\,d\eta\,d\phi,$$

where ϱ is the internuclear distance of the hydrogen-fluorine bond under consideration.

$$S_N = C_F(2s)\frac{1}{2\pi}\frac{\varrho^3}{8}\int_0^{2\pi} d\phi \int_{\xi=1}^{\infty}\int_{\eta=-1}^{+1}\left\{r_{1B}-\frac{\varrho}{2}(\xi-\eta)\right\}$$

$$\times(\xi^2-\eta^2)\sum_{m=1}^{3} A_m \exp\left(-\xi\,\tfrac{1}{2}\varrho\,(a_m+1)-\eta\,\tfrac{1}{2}\varrho\,(a_m-1)\right)d\xi\,d\eta$$

$$= C_F(2s)\frac{\varrho^3}{8}\sum_{m=1}^{3} A_m\{r_{1B}\,(A_2(\gamma_m)\cdot B_0(\delta_m)-A_0(\gamma_m)\cdot B_2(\delta_m))$$

$$-\tfrac{1}{2}\varrho\,((A_3(\gamma_m)\cdot B_0(\delta_m)+A_0(\gamma_m)\cdot B_3(\delta_m)-A_1(\gamma_m)\cdot B_2(\delta_m)-A_2(\gamma_m)\,B_1(\delta_m))\}$$

$$= K_N\sum_{m=1}^{3} A_m \sum_{\lambda=1}^{2} c_\lambda\,[A_\mu(\gamma_m)\cdot B_\nu(\delta_m)]_\lambda$$

which is of the form given above. The parameter tape will contain the values of N, K_N, $k_\varkappa$, c_λ, μ and ν, $\gamma_\varkappa$ and $\delta_\varkappa$ together with some parameters giving the sign of the terms in the integral.

Using the expression for the overlap, it is easy to write down the corresponding moment integral. As shown in appendix II the moment integral M_N is related to the overlap integral $S_N(A_\mu(\gamma)\cdot B_\nu(\delta))$ in the following way

$$M_N = \tfrac{1}{2}\varrho\, S_N(A_{\mu+1}(\gamma)\cdot B_{\nu+1}(\delta)).$$

Because of this very simple relationship the program has been extended automatically to perform the computation of the moment integral from the parameter values given for the overlap integral. In a program used for the calculation of molecular dipole moments (to be published), the procedure saved half of the stamping work. The computations of overlap and moment integrals involving s and p functions according to this program have been carried out on the Swedish electronic computer BESK at the Swedish Board for Computing Machinery (MNA) in Stockholm, where the program is available under the designation IM1/0732. The program is, of course, not restricted to the use of SCF functions, but can equally well be applied to Slater functions. In the latter case, however, a more convenient program, extremely simple in use, has been devised by Flodmark [10] and recently presented in this journal. It is available at MNA under the notation S 3.

APPENDIX I

Additional data regarding the program

A single precision (9 place) floating point interpretive routine named Flinta was utilized in the program. This diminished the space available in the computer, causing the following limitations to be imposed on the number of the quantities used:

Maximum number of $k_\varkappa$, $\gamma_\varkappa$ and $\delta_\varkappa$ values $=48$ different of each
c_λ values $=18$ different
$A_\mu(\gamma)$ and $B_\nu(\delta)$ integrals $=10$ of each $(0 \leqslant \mu, \nu \leqslant 9)$

The limitations set to μ and ν, essentially introduced to avoid the use of sedecimal numbers, give rise to the restrictions on $n_A + n_B$ given in the text.

Computation of $A_\mu(\gamma)$ and $B_\nu(\delta)$

$A_\mu(\gamma)$ was computed with the aid of the following relationship

$$A_\mu(\gamma) = \frac{\mu}{\gamma} A_{\mu-1}(\gamma) + A_0(\gamma).$$

In computing the $B_\nu(\delta)$ integral, two types of formulae were necessary as mentioned in the text

$$B_\nu(\delta) = \frac{\nu}{\delta} B_{\nu-1}(\delta) + \frac{(-1)^\nu \cdot e^\delta - e^{-\delta}}{\delta} \qquad |\delta| > 4$$

$$\begin{cases} B_\nu(\delta) = \quad 2\left\{\dfrac{1}{\nu+1} + \dfrac{\delta^2}{2!\,(\nu+3)} + \dfrac{\delta^4}{4!\,(\nu+5)} + \cdots\right\} & \nu \text{ even}, \quad |\delta| \leqslant 4 \\ B_\nu(\delta) = -2\left\{\dfrac{\delta}{\nu+2} + \dfrac{\delta^3}{3!\,(\nu+4)} + \dfrac{\delta^5}{5!\,(\nu+6)} + \cdots\right\} & \nu \text{ odd}, \quad |\delta| \leqslant 4 \end{cases}$$

As can be seen the value $|\delta|$ has been used instead of the correct one $|\delta/\nu|$ as a criterion for the choice of formula to be employed in computing $B_\nu(\delta)$. This approximation, however, was found to be quite satisfactory.

APPENDIX II

Referring to the example in the text the contribution to the overlap integral can be written

$$S_N = \int \psi_A \psi_B \, d\tau = 2\pi \int_{\xi=1}^{\infty} \int_{\eta=-1}^{1} g(\xi,\eta) \sum_\varkappa k_\varkappa \exp(-\xi\gamma_\varkappa - \eta\delta_\varkappa) \, d\xi \, d\eta$$

$$= S_N(A_\mu(\gamma) \cdot B_\nu(\delta)).$$

From Fig. 1, $z = z_A - \frac{1}{2}\varrho$. Introducing $z_A = r_A \cos\vartheta_A = \frac{1}{2}\varrho\,(1+\xi\eta)$ giving $z = \frac{1}{2}\varrho\,\xi\eta$, the corresponding moment integral is expressed by

$$M_N = \int \psi_A z \psi_B \, d\tau = \frac{\varrho}{2} 2\pi \int_{\xi=1}^{\infty} \int_{\eta=-1}^{1} \xi\eta \cdot g(\xi,\eta) \times \sum_{\varkappa} k_\varkappa \exp\left(-\xi\gamma_\varkappa - \eta\delta_\varkappa\right) d\xi\, d\eta = \frac{\varrho}{2} \cdot S_N\left(A_{\mu+1}(\gamma)\cdot B_{\nu+1}(\delta)\right).$$

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Ing. Harald Tydén of the Swedish Board for Computing Machinery, who coded the program. The free machine time granted by the Swedish Board for Computing Machinery and the financial support provided by the Swedish Atomic Committee, the Swedish Natural Science Research Council and the State Council of Technical Research are gratefully acknowledged. The nuclear magnetic resonance research which initiated the present calculations was made possible by a generous grant from the Knut and Alice Wallenberg Foundation.

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Tryckt den 8 december 1960

Uppsala 1960. Almqvist & Wiksells Boktryckeri AB